Importance of protein cross-linking and disulfide reduction for the mechanical properties of compression molded rigid wheat gluten bioplastics

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Introduction

Wheat gluten, available in large quantities as co-product of the industrial gluten-starch separation, is an interesting raw material for the production of biobased materials [1]. In absence or at low concentrations of plasticizer, high-temperature compression molded wheat gluten vitrifies into a rigid, glassy material upon cooling [2]. Both strength and failure strain of rigid glassy materials increase with increasing molding temperature, which corresponds to an increased degree of cross-linking [2]. Different types of gluten cross-links can be present in rigid, glassy gluten materials, but disulfide bonds are predominant [3]. Additives containing thiol (SH) groups can be used to improve the mechanical properties of rigid gluten materials. Whereas for some additives the enhanced properties could be related to an increased degree of cross-linking, this seems not always the case [4, 5]. The aim of this research was to investigate the effect of SH and disulfide containing additives on gluten cross-linking and to establish the impact of the additive-induced gluten network modifications on the mechanical properties of rigid gluten materials.

Experimental

Commercially available polyols [tris(hydroxymethyl)ethane (THME), polyglycerol (PG) and hybrane (H1500)] were SH functionalized by esterifying (part of) their hydroxyl groups with the carboxyl group of 3-mercaptopropionic acid (MPA) as described in [5]. Oxidized functionalized H1500 (oxfH1500) was obtained by treating SH functionalized H1500 (fH1500) with N-bromosuccinimide. After the oxidation procedure all SH groups were oxidized to disulfide groups.

Gluten was mixed with the different functionalized additives as well as with MPA in 95% ethanol and via extrusion. Subsequently, the mixed samples were compression molded at 130 °C [2]. After molding, the mechanical properties were determined with a 3-point bending test. The effect of the additives on the gluten network after mixing and molding was evaluated by determining the level of extractable protein with sodium dodecyl sulfate (SDS) containing medium (SDSEP) and by measuring the level of free SH [3].

Results and discussion

The effect of SH functionalized additives on flexural strength of rigid gluten materials depended on the mixing system. All non-oxidized SH containing additives (MPA, fTHME, fPG, and fH1500) improved the strength compared to a reference sample, both after mixing in 95% ethanol and after extrusion. Similar strengths were obtained with all non-oxidized additives when extrusion was used as a mixing system, whereas the improvement in strength with MPA and fTHME was higher than that with fPG and fH1500 when gluten was mixed with the additives in 95% ethanol.

Overall, samples containing additives with multiple SH groups have a lower SDSEP content, and thus higher degree of cross-linking after molding than gluten with the monothiol MPA. However, the strength with such additives was either similar to or lower than that of samples with MPA. This demonstrates that the degree of cross-linking is not the only factor that determines the strength of rigid, glassy gluten materials. While SH containing additives improved the mechanical properties, oxfH1500 had no effect on the strength, even though it also affects the cross-linking. It appears that the presence of SH groups is important for the improvement of the mechanical properties with additives.

The SDSEP data after mixing of the samples showed that all additives with SH groups had a reducing effect during mixing, which was not the case for oxfH1500. Interestingly, only when a strong reducing effect was observed during mixing (e.g. with MPA), a high strength was obtained after molding. It seems that reduction of gluten during mixing with additives is more important to obtain the highest strength than the impact of the additive on the cross-linking occurring during molding. This supports our view that besides cross-linking, also altered molecular conformations and improved entanglements contribute to the strength [5].

Conclusions

Flexural strength of rigid gluten materials can be improved with SH containing additives, whereas additives with only disulfide functionality have no effect on these mechanical properties. Both additives with SH and disulfide functionality affect the cross-linking during processing. However, our results demonstrate that the degree of cross-linking is not the only factor that determines the strength of rigid, glassy gluten materials. Mechanical properties were improved when additives acted as a reducing agent during mixing. In our view besides cross-linking, also altered molecular conformations and improved molecular entanglements contribute to the strength.

References

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